

SEPARATOR DEVELOPMENT
FOR A HEAT STERILIZABLE BATTERY
Quarterly Summary Progress Report 3

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ABSTRACT

The following three types of ligand containing polymers are being developed for use as separator materials in sterilizable silver-zinc batteries:

- (1) Styrene-maleic anhydride copolymers;
- (2) Styrene-maleic anhydride-methyl methacrylate terpolymers; and
- (3) 40:60 2-vinylpyridine-methyl methacrylate copolymer.

The mechanical strength and flexibility of our styrene-maleic anhydride copolymer films has been significantly improved by using uniformly high molecular weight materials.

The terpolymers have excellent film properties and are being modified to lower electrical resistivity in 40% KOH. Polymers with higher contents of hydrolyzable acrylate and anhydride groups, were prepared. Insoluble polymers of this type had resistivities from 35 to 70 ohm-in. after sterilization. Polymers with very high hydrolyzable contents had some solubility in electrolyte and are being modified by crosslinking to make them insoluble.

Reaction conditions for preparation of the 40:60 2-vinylpyridine-methyl methacrylate polymer were studied to increase their molecular weight. Polymerization to high conversions gave significant increases in molecular weight.

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I. INTRODUCTION

The primary objective of this program is the development of highly stable battery separator materials that will function satisfactorily in a sealed Ag-Zn secondary battery after heat sterilization at 135°C, and have sufficient flexibility and mechanical strength so that they can be incorporated into the battery system by practical fabrication techniques. Three types of ligand-containing polymers that showed a great deal of promise for use as heat sterilizable separators for the Ag-Zn cell in preliminary tests in our initial JPL 951524 program are now being developed. These are:

1. Hydrolyzed copolymers of 2-vinylpyridine-methyl methacrylate and of styrene-maleic anhydride;
2. Hydrolyzed styrene-maleic anhydride-methyl methacrylate terpolymers;
3. Styrene copolymers containing 8-hydroxyquinoline substituents.

During this report period our objectives were as follows:

1. Determine the molecular weight range for styrene-maleic anhydride copolymers with the best mechanical properties and film-forming ability;
2. Improve the electrical properties of the styrene-maleic anhydride-methyl methacrylate terpolymers;
3. Prepare films and evaluate the electrical and mechanical properties of high molecular weight styrene-maleic anhydride copolymers and the terpolymers;
4. Study the reaction conditions for preparation of the 40:60 2-vinylpyridine-methyl methacrylate copolymer to increase its molecular weight.

II. SUMMARY

The following three types of ligand-containing polymers which showed promise as battery separator materials for sterilizable silver-zinc cells in our initial program are now being further developed:

1. Styrene-maleic anhydride copolymers;
2. Styrene-maleic anhydride-methyl methacrylate terpolymers;
3. 40:60 2-vinylpyridine-methyl methacrylate copolymers;

The usefulness of the styrene-maleic anhydride copolymer was previously limited because the low molecular weight samples that were used gave hard, brittle films in a dry atmosphere. High molecular weight samples of this copolymer having intrinsic viscosities of 4.3 and 1.8, compared to 0.8 for the earlier samples, were prepared. These polymers formed films with much greater flexibility and also slightly higher tensile strength. The polymer with 1.8 intrinsic viscosity has better film-forming properties than the highest molecular weight polymer, because of higher solubility in the casting solvent.

The styrene-maleic anhydride-methyl methacrylate terpolymers used before gave films with good mechanical properties, but had electrical resistivities after sterilization that were close to the usable maximum of 60 ohm-in. Several terpolymers were prepared from reactants containing a high ratio of maleic anhydride. It was necessary to prepare these polymers in methylene chloride solvent to obtain high molecular weights. The strong azeotropic effect in polymerization of these monomers limited their anhydride content to under about 40%. For this reason, other modifications of these polymers were made to obtain larger improvements in their electrical properties than could be realized from this polymer composition.

The major modification was to incorporate easily hydrolyzable methyl acrylate units in the polymer to make tetrapolymers. These polymers were readily prepared by bulk polymerization and had slightly higher molecular weights than the terpolymers. Sample films of tetrapolymers prepared from 43:25:10:22 and 48:25:10:17 charges of styrene-maleic anhydride-methyl methacrylate-methyl acrylate had electrical resistivities from 35 to 70 ohm-in. after sterilization in 40% KOH. Films of tetrapolymers from charges containing high contents of hydrolyzable anhydride and acrylate groups, that should have lower resistivities, could not be tested because of some solubility in 40% KOH after sterilization. These polymers are being modified by incorporation of 2-chloroethylvinyl ether units, which will act as sites for crosslinking the polymers during film formation to make them insoluble.

The reaction conditions used to prepare the 40:60 2-vinylpyridine-methyl methacrylate copolymer were studied in an effort to increase its molecular weight. The polymer is prepared by bulk polymerization of a 30:70 monomer charge. Reaction variables that were studied include temperature, catalyst concentration, and degree of conversion. Polymers with significantly higher molecular weight were obtained at high conversions, indicating that coupling is the major mode of chain termination for this polymer.

III. DISCUSSION OF RESULTS

A. PREPARATION OF POLYMERS

1. Styrene-Maleic Anhydride Copolymer

We had found previously (ref. 1) that films of Lytron® 810, styrene-maleic anhydride copolymer, had excellent electrical properties for a battery separator material, but were hard and had low flexibility in dry atmospheres. This copolymer has a molecular weight of about 50,000. Therefore, copolymers with higher molecular weight were prepared to improve these mechanical properties in the styrene-maleic anhydride films. One copolymer was prepared by polymerization of the monomers in methylene chloride solution, following a method developed by Hibbard (ref. 2). The product has an intrinsic viscosity of 4.3 compared to 0.8 for the Lytron 810 resin. Small samples of films prepared from this polymer have much greater flexibility than similar films made from Lytron 810 copolymer. However, it is difficult to prepare films of this polymer with thicknesses over 0.4 mil, because of its low solubility.

Therefore, two polymers with molecular weights intermediate between Lytron 810 copolymer ($[\eta] = 0.8$) and this high molecular weight copolymer 99119 ($[\eta] = 4.3$) were prepared by polymerization in methylene chloride containing β -nitrostyrene as chain terminator (Table 1). Polymers prepared with 0.015 and 0.048% terminator had approximately the same molecular weight ($[\eta] = 1.8$). These polymers had better film forming properties than polymer 99119.

2. Styrene-Maleic Anhydride-Methyl Methacrylate Terpolymers

A series of polymerizations with the above monomers was run to determine the best reaction conditions for preparation of high molecular weight terpolymers with high maleic anhydride content. Two general reaction procedures were used:

1. Polymerization in bulk at 60°C in nitrogen atmosphere with 0.02 weight % azo-bis-isobutyronitrile catalyst;
2. Polymerization in refluxing 5% methylene chloride solution with either lauroyl peroxide or azo-bis-isobutyronitrile catalyst.

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Table 1

COMPOSITION OF STYRENE-MALEIC ANHYDRIDE COPOLYMERS
AND STYRENE-MALEIC ANHYDRIDE-METHYL METHACRYLATE TERPOLYMERS

Reference	Mole Ratio Monomers St:MA:MMA	Solvent	Catalyst* g/100g Monomer ^a	Temp °C	Reaction Time, Hrs.	Conversion wt-%	η_r for 0.5% Solution	Estimated MA in Polymer wt-%	Estimated Mole Ratio of Monomers in Polymer
99119	50:50:0	MC**	0.60 LP	42	20	70	4.51	--	(50:50:0)
99130A	50:50 with 0.015% -nitro- styrene	MC	0.60 LP	42	20	59	2.00	--	(50:50:0)
99130B	50:50 with 0.048% -nitro- styrene	MC	0.60 LP	42	20	56	2.20	--	(50:50:0)
99109A	33:33:33	None	0.02 ABIN	60	1	11	1.08	31	41:32:27
99111C	20:40:40	None	0.02 ABIN	60	1	14	1.04	31	42:32:25
99109B	30:50:20	None	0.02 ABIN	60	1	20	1.08	30	46:31:23
99111D	20:50:30	None	0.02 ABIN	60	1	24	1.03	36	30:37:32
99113A	50:25:25	None	0.02 ABIN	60	1	10	2.65+	34	44:35:21
99118	18:50:32	MC	0.60 LP	42	20	19	1.51	32	39:33:28
99115	33:33:33	MC	0.60 LP	42	20	28	1.81	34	
99116	33:33:33	MC	2.0 ABIN	42	26	28	1.27	32	
99117	40:45:15	MC	0.60 LP	42	6	8	1.65	34	40:35:25
99121	50:25:25	MC	0.60 LP	42	19	22	1.86+	32	
99122	50:25:25	MC	1.80 ABIN	42	19	22	1.32+		
99124	51:24:25	MC	0.30 LP	42	20	14	1.64		
99125	51:24:25	MC	0.90 ABIN	42	40	18	1.36		

* ABIN = azobisisobutyronitrile; LP = lauroyl peroxide

** MC = methylene chloride

† η_r of duplicate composition in bulk preparation was 1.53 (sample 10024A)

The data obtained are in Table 1. These data can be summarized as follows:

1. Variations in the ratio of reactants result in only small changes in polymer composition due to a very marked azeotropic effect;
2. Variations in the ratio of reactants markedly effects that rate of polymerization in bulk. For example, increasing the ratio of maleic anhydride to styrene by a factor of 2 1/2 in the charge doubled the rate of reaction;
3. Monomer charges with high ratios of maleic anhydride to styrene gave polymers with low degrees of polymerization, in bulk reactions, but gave polymers that have high degrees of polymerization and form usable films, in solution polymerizations in methylene chloride;
4. In the solution polymerizations, lauroyl peroxide catalyst consistently yielded polymers with slightly higher molecular weights than those prepared with the azo catalyst.

An attempt was also made to prepare styrene-fumarate-methyl methacrylate terpolymers (Table 2). These monomers saponify to dicarboxylic acids and have copolymerization reactivity ratios with styrene (ref. 3) that should allow production of polymers with appreciable fumarate contents. However, the reactivity of both diethyl fumarate and monoethyl fumarate is extremely low and polymerization in methylene chloride was impracticably slow. Also, a viscosity determination of the terpolymer containing the monoethyl fumarate indicated that its molecular weight was not high enough to give mechanically strong films.

3. Styrene-Maleic Anhydride-Methyl Methacrylate-Methyl Acrylate Tetrapolymers

The styrene-maleic anhydride-methyl methacrylate terpolymers were modified by adding methyl acrylate units to lower electrical resistivity in 40% KOH by increasing the content of hydrolyzable groups. Several polymers with different ratios of the four monomers were prepared by bulk polymerization. Data describing these polymers are in Table 2. Viscosity measurements show that the molecular weights of these polymers are slightly higher than those of the terpolymers.

In our tests of separators made from these polymers (see Section III, B) we found that polymers with high contents of the hydrolyzable anhydride and acrylate groups had high solubility in 40% KOH. Since this type polymer should have the best electrical properties, they are being modified by introduction of sites for crosslinking. These linear polymers will then be crosslinked

Table 2

COMPOSITION OF STYRENE-MALEIC ANHYDRIDE-METHYL METHACRYLATE-METHYL ACRYLATE TETRAPOLYMERS AND MODIFICATIONS

Reference	Mole Ratio Monomers* St:MA:MMA:X	Solvent**	Catalyst*** g/100g Monomer	Temp °C	Reaction Time, Hrs.	Conversion wt-%	η_{sp} for 0.5% Solution
99123	15:0:25:60 DEF	MC	0.70 LP +	42	60	under 3	---
99133	19:0:30:51 EF	MC	1.0 LP +	42	25	10	1.06
99127	43:25:10:22 MAC	None	0.02 ABIN	60	2	22	2.60
99138B	43:25:10:22 MAC	None	0.02 ABIN	60	2	10	2.76
99128	17:30:20:33 MAC	MC	0.60 LP	42	40	15	1.33
99129	48:25:10:17 MAC	None	0.02 ABIN	60	1.7	22	2.24
99132	28:20:19:33 MAC	None	0.02 ABIN	60	3	over 50	4.8
99137	18:29:9:44 MAC	None	0.02 ABIN	60	2	11	2.59
99138C	18:29:19:33 MAC	None	0.02 ABIN	60	2	12	3.28
99142D	28:20:19:33 MAC	None	0.02 ABIN	60	1.5	10	2.15
99142E	28:20:19:33 MAC+	None	0.02 ABIN	60	3.5	7.6	1.77
99145	28:20:19:33 MAC+	None	0.02 ABIN	60	3.5	27	1.89
99146	28:20:19:33 MAC++	None	0.02 ABIN	60	10	18	1.66

* MAC is methyl acrylate, DEF is diethyl fumarate and EF is monoethyl fumarate

** MC is methylene chloride

*** ABIN is azobisisobutyronitrile; LP is lauroyl peroxide

+ Plus 5 weight % 2-chloroethylvinyl ether

++ Plus 10 weight %

during film formation to reduce solubility in 40% KOH. 2-Chloroethylvinyl ether is being used as a site for the crosslinking reaction. Three polymers (99142E, 99145 and 99146 in Table 2) have been prepared by bulk copolymerization of 5 or 10 weight % 2-chloroethylvinyl ether with the monomers in a standard tetrapolymer. The chloroethyl substituted monomer caused only a moderate decrease in rate and degree of polymerization of these polymers. The products are now being analyzed for chloride.

4. 40:60 2-Vinylpyridine-Methyl Methacrylate Copolymer

A study of the reaction conditions used to prepare this polymer to increase polymer molecular weight was started. The polymerizations were carried out in pressure bottles. A 30 to 70 mole ratio of the monomers, 2-vinylpyridine and methyl methacrylate, together with azo-bis-isobutyronitrile catalyst were charged to the bottles and flushed with nitrogen. The bottles were then sealed and shaken in a bath at controlled temperature. The products were isolated by precipitation with hexane and purified by three successive reprecipitations using toluene/hexane as the solvent/precipitant combination.

The following reaction conditions were varied:

- a. temperature (40, 60°C);
- b. amount of catalyst (to give rate of initiation equivalent to 0.02 and 0.005 wt% at 60°C);
- c. conversion (10-20, 40, 60).

The results of polymerizations done so far are given in Table 3. Polymers with significantly higher molecular weights were obtained by polymerization to conversions above 35%, indicating that coupling is a major mode of chain termination for this polymer.

The results also indicate that lowering the reaction temperature appears to give a slight increase in molecular weight. However, more data are needed to determine the exact magnitude of this effect. The variations in rate of initiation that were made in runs at 60°C gave no significant change in the molecular weight of the product.

B. EVALUATION OF SEPARATOR PROPERTIES

Evaluation of films prepared from styrene-maleic anhydride copolymers and from styrene-maleic anhydride-methacrylate ter- and tetrapolymers as separator materials for the silver-zinc cells was started. The films were prepared by casting filtered solutions of the polymers in methyl ethyl ketone onto polypropylene

Table 3

EFFECT OF VARIATIONS IN POLYMERIZATION CONDITIONS ON PROPERTIES OF 40:60
2-VINYLPYRIDINE-METHYL METHACRYLATE COPOLYMER (a)

Reference	Catalyst, (b) g/100g Monomers	Temp, °C	Reaction Time, Hours	Conversion, Wt%	η_R for 0.5% (c) Soln of Polymer	Mole Ratio 2-VP:MMA in Polymer (d)
58019	0.02	60	7	7	1.53	38:62
58024	0.02	60	14	40	1.93	35:65
58021	0.02	60	21	40	2.11	36:64
58022	0.005	60	24	7	1.54	39:61
58038	0.005	60	88	18	1.56	
58027	0.40	40	16	16	1.72	40:60
58036	0.40	40	40	72	2.46	36:64
58037	0.10	40	79	39	2.48	38:62

(a) Mole ratio monomers charged 2-VP:MMA; 30:70

(b) Azo-bis-isobutyronitrile

(c) In dimethylformamide at 30°C

(d) Calc. from analysis for pyridine content by method in ref. 2.

sheets, leveling with a Gardner blade and drying in an oven at 35°C. The concentration used for polymers with η_R of 2 at 0.05% was about 8%. The concentration of polymer 99119 was about 3%.

The following film properties are being measured to determine stability and durability in 40% KOH at 135°C, electrical resistivity in 40% KOH, and mechanical strength when dry and when soaked in electrolyte:

1. dimensions;
2. electrolyte absorption;
3. electrical resistance;
4. appearance;
5. tensile strength.

The procedures used to measure these properties were described before in our Summary Report (ref. 1). Tensile strength determinations made of dry and soaked films are in Table 4 and the electrical properties of sterilized films are in Table 5.

The initial determinations of tensile strength show that the tetrapolymers have strengths comparable to the terpolymers and higher than the copolymers. The higher molecular weight styrene-maleic anhydride polymers have slightly higher tensile strengths than Lytron 810 copolymer (ref. 1) in addition to having much greater flexibility and bendability when dry.

The durability of the films in 40% KOH was tested by sterilization at 135°C for 64 hrs. Several films were also sterilized in 40% KOH containing 1M ZnO to determine the effect of the zincate ions on the electrical properties of the separators. The properties of the sterilized films can be summarized as follows:

1. Acceptably low (under 60 ohm-in.) electrical resistivities were obtained from sterilized separators made from most of the styrene-maleic anhydride-methyl methacrylate terpolymers and styrene-maleic anhydride-methyl methacrylate-methyl acrylate tetrapolymers as well as the styrene-maleic anhydride copolymers.

2. Tetrapolymers with high contents of hydrolyzable groups (99132, 99138B, 99138C, 99137) that should have lower electrical resistivities dissolved in electrolyte during sterilization. Two terpolymers, 99117 and 99118, also partially dissolved during sterilization. This suggests that the anhydride content of these polymers is higher than was found by direct titration for acid equivalent.

Table 4

TENSILE STRENGTH OF MEMBRANES AT ROOM TEMPERATURE

Polymer No.	Polymer Composition	Film State	Number of Specimens	Elongation at Break, %	Tensile Strength(psi)
99115	Styrene-maleic anhydride-methyl methacrylate terpolymer from 33:33:33 Monomer charge	dry	2	3 (2)*	5000
		wet after soaking in 40% KOH 1 week at room temp.	4	1 (5)	1180
99128	Styrene-maleic anhydride-methyl methacrylate-methyl acrylate tetrapolymer from 17:30:20:33 charge	dry	3	2 (0.5)	4850
99127	Styrene-maleic anhydride-methyl methacrylate-methyl acrylate tetrapolymer from 43:25:10:22 charge	dry	4	3 (2 and 0.5)	2750
		wet after soaking in 40% KOH 1 week	5	1 (0.5)	975
99119	Styrene-maleic anhydride copolymer ($[\eta] = 4.3$)	dry	1	1 (0.5)	3750
99130B	Styrene-maleic anhydride copolymer ($[\eta] = 1.8$)	wet after soaking in 40% KOH 1 week	2	130 240 (0.5)	770 670

* value in parenthesis is crosshead speed, in inches/min., used in test.

Table 5

PROPERTIES OF SEPARATORS AFTER STERILIZATION IN 40% KOH AT 135°C

Polymer No.	Polymer Composition	Properties after Sterilization for 64 Hours					Appearance
		Dry Thickness(mils)	Thickness(mils)	Wt. Gain(%)	Area Retention(%)	ρ (ohm-in)	
99119	Styrene-maleic anhydride copolymer	0.69	1.8	228	(100)**	40.2*	Sl. yellow
		0.65	3.1	283	35	32.9	Shrunken
		0.65	1.1	350	70	----	
99130B	Styrene-maleic anhydride copolymer	1.16	2.26	192	(100)	39.4	Uneven surface
		1.1	1.5-3.8	296	64	(0.091 ohm-in ²)	
		0.93	1.5	174	(100)	55.7*	
99121	Styrene-maleic anhydride-methyl methacrylate terpolymer from 50:25:25 monomer charge	0.54	1.36	488	100	21	Some surface wrinkles
		0.92	2.66	207	100	34	
99117	Same as 99121 but from 40:45:15 monomer charge	0.47	film continuity lost during sterilization				
		0.49					
99118	Same as 99121 from 18:50:32 monomer charge	0.04	0.36	1000	film continuity lost during sterilization		
99115	Same as 99121 from 33:33:33 monomer charge	1.7	3.4	244	(100)	49.2*	
99127	Styrene-maleic anhydride-methyl methacrylate-methyl acrylate polymer from 43:25:10:22 charge	0.9	2.5	248	100	37.9	Wrinkled
		1.6	3.3	227	---	35.7*	Brown colored
		1.18	1.6	171	(100)	70.7	
99129	Same as 99127 from 48:25:10:17 charge	1.34	2.2	178	(100)	40.5	
		1.6	2.7	200	(100)	33.0*	
		2.1	2.8	189	105	49.7	
		1.0	2.6	258	77	37.9	
		1.2	3.9	335	90	----	
99137	Same as 99127 from 18:29:9:44 monomer charge	1.1	2.7	99	100	86*	
			film continuity lost				
99138C	Same as 99127 from 18:29:19:33 monomer charge	0.73	---	360	film continuity lost		
99132	Same as 99127 from 28:20:19:33 charge	film continuity lost					

* Sterilized in 40% KOH containing 1M ZnO

** (100) indicates that area was controlled by fastening sample to Teflon frame with Teflon plugs

3. Polymer samples that had low electrolyte absorption had the highest resistivities, as expected. The causes of the relatively large variations in electrolyte absorption found for different samples of the same polymer (e.g. 207 and 488% for 99121) are not completely known. In some cases, we have found that samples fastened onto Teflon cylinders (one exposed surface) absorb less electrolyte than samples exposed in Teflon frames (two exposed surfaces) and therefore, all samples are now sterilized in Teflon frames.

4. Several samples were held in the Teflon frames by inserting Teflon plugs through both the separator sample and the frame. Samples of polymers 99119, 99130B, 99115 and 99127 that were sterilized in this way maintained surface dimensions well without formation of any cracks or other imperfections from strain stresses. This indicates that dimensional changes in the separator caused by structural changes in the polymer during hydrolysis can be controlled easily.

C. ANALYSIS OF POLYMERS

1. Styrene-Maleic Anhydride-Methyl Methacrylate Terpolymers

The composition of these polymers was determined from their elemental analysis for carbon and hydrogen, together with their neutralization equivalents. The method used to measure neutralization equivalents was described before (ref. 1).. Lytron 819 copolymer gave a correct analysis by this method. However, the high molecular weight copolymer 99119 analyzed only 80% of theoretical based on a 1:1 copolymer.

The neutralization equivalents reported in Table 1 are those found from this titration. Values found from elemental analysis also indicate that maleic anhydride contents of the terpolymers are under 40% and that compositions of all polymers are very similar.

Some improvement in the accuracy of this method with the higher molecular weight samples was obtained by adding 1g of sodium chloride to each sample. The presence of the sodium ion made the end point sharper and the accuracy of analysis of copolymer 99130B, assuming 1:1 copolymer composition, was 92%.

Attempts to measure composition of the terpolymers from the absorptions in the infrared of the α -methyl and ester groups of the methyl methacrylate component and the anhydride groups of the maleic anhydride component in terpolymer samples were not successful. Two measures of absorption were determined. The band heights of these absorptions were not reproducible. The band areas gave composition values that did not correlate

with compositions of polymers that were determined from neutralization equivalents and elemental analysis. Adjacent absorption bands from the styrene component of the terpolymers apparently interfered with this measure.

2. Styrene-Maleic Anhydride-Methyl Methacrylate-Methyl Acrylate Tetrapolymers

Because of the large number of components in these polymers, analysis has been limited to determination of hydrolyzable groups. Neutralization equivalents, using the sodium chloride modification of the procedure described above, were determined to measure anhydride content. We are also attempting to determine acrylate content from saponification equivalents. The methacrylate groups are considered non-hydrolyzable, since they do not saponify in these polymers under mild saponification conditions.

Samples of the tetrapolymers were saponified by heating overnight at 85°C in standardized 2N NaOH in pressure bottles to convert the anhydride and acrylate groups to their salts. The polymers dissolved during saponification. However, it was not possible to determine reproducible titres by direct titration with acid or back titration with base after acidification because of incomplete reaction near the end point caused by precipitation of the polymer near the neutralization point.

3. 2-Vinylpyridine-Methyl Methacrylate Copolymer

Composition of these copolymers was readily determined by titration with perchloric acid in acetonitrile-acetic acid solvent. The method developed by Tamikado (ref. 4) was used. Polymers that analyzed 45 and 32 mole % 2-vinylpyridine from elemental nitrogen determinations, analyzed 39.5 ± 1.5 and 29.2 ± 0.4 mole %, respectively, by this titration method.

The use of measures of refractive index of solutions of these polymers as an analytical method was also tried. This method has been used for analysis of styrene-methyl methacrylate copolymers (ref. 5). However, we found that the difference in refractive index between methyl ethyl ketone solutions of 2-vinylpyridine-methyl methacrylate copolymers with 40 and 20 mole % 2-VP was too small to detect the differences in polymer composition.

IV. PROGRAM PLAN

A. GENERAL

The overall approach to be followed in accomplishing our contract objectives can be divided into the following five phases:

1. Optimization of copolymers;
2. Optimization of terpolymers;
3. Development of new separator materials;
4. Comprehensive tests;
5. Preparation of film samples.

Our long-range program planning chart showing the proposed distribution of effort for each of these phases is given in Table 6.

B. ANTICIPATED WORK FOR NEXT QUARTER

1. Complete the study of the effect of reaction parameters on molecular weight of the 40:60 2-vinylpyridine-methyl methacrylate copolymer.

2. Develop methods to crosslink both the 2-vinylpyridine-methyl methacrylate copolymers and the styrene-maleic anhydride-methyl methacrylate-methyl acrylate tetrapolymers during film formation.

3. Determine the degree of crosslinkage necessary to insolubilize tetrapolymers with high maleic anhydride-methyl acrylate contents in 40% KOH.

4. Evaluate the electrical and mechanical properties, before and after sterilization, of films prepared from the modified polymers.

Table 6

OVERALL PROGRAM PLANNING CHART

<u>Program Phase</u>	<u>Per Cent of Total Research Effort</u>										
	<u>July</u>	<u>Aug</u>	<u>Sept</u>	<u>Oct</u>	<u>Nov</u>	<u>Dec</u>	<u>Jan</u>	<u>Feb</u>	<u>March</u>	<u>April</u>	<u>May</u>
Optimization of copolymers	10	35	40	40	30	20					
Optimization of terpolymers	90	60	55	55	40						
Development of new separator materials							25	40	80	10	
Comprehensive tests		5	5	5	5	5	10	10	5	40	
Preparation of film samples					25	50	50	10	85	40	
Final report										20	100

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